

Electrically Conducting Polyaniline Microtube Blends

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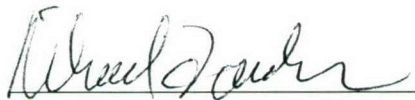
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Michael Zambrana
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14. ABSTRACT Self-assembled polyaniline micro/nanotubes were synthesized by a template-free method. Changing the molar doping level ratio [Aniline]:[dopant] from 0.25 to 2 increased the polyaniline tube (PAT) diameter by 3 orders of magnitude. Bulk conductivity of the tubes was demonstrated for both micro- and nanotubes and varied from 0.01 to 1.2 S/cm. When microtubes were solution-blended with polyurethane, a highly dispersed fractal network of tubes was observed, and the resulting blend conductivity was 1×10^{-5} S/cm and 1×10^{-3} S/cm for 0.5% and 2% (wt/wt) PANI microtube loadings, respectively. These values were sufficient for the minimal value needed (1×10^{-6} S/cm) for charge mitigation. The promising results of this program lend themselves to developing an all-polymer microtube-conducting composite that has sufficient conductivity and transparency to mitigate electrical charge in lightweight space structures.					
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1. Introduction

Electrically conducting polymers, recently described by the Nobel Laureate Alan J. Heeger as the “fourth generation of polymeric materials,”¹ have provided an alternative to traditional intrinsically conducting materials such as carbon black and metallic particulates. Intrinsically conducting polymers (ICP) embody both the electrical and optical properties found in metals and inorganic systems. The focus of this work is to develop and characterize an intrinsically conductive polymer system to mitigate electrical charge buildup in large, ultra-lightweight structures for deployable space applications. A number of different approaches to fabricate these polymer structures has been published,^{2,3} yet a simple and effective process still remains elusive. Current efforts in this area by NASA Langley⁴ have blended single-walled carbon nanotubes (SWCN) with polyimide (PI) to achieve anti-static behavior. In addition to using nanotechnology as a means to mitigate surface conductivity, older technologies such as metal fillers⁵ and carbon black impart conductivity to polymer blends,⁶ but their high loading fraction (>20%, wt/wt) makes them impractical for applications that require high transmissivity. In contrast to adding conducting particulates (i.e., SWCN, carbon black, etc.) to induce conductivity, the use of ICPs is an emerging new technology that is gaining acceptance because of the relatively high bulk conductivity of the resulting blend and the minimal impact on the mechanical and optical properties of the host. Therefore, the challenge lies in successfully synthesizing a conducting polymer, coupled with the necessity to disperse the ICP to maximize both optical and conducting properties necessary for mitigating electrical charges in lightweight space structures. The synergetic effect of blending an ICP with a host is a promising, novel approach for mitigating electrical charge buildup in these deployable space applications.

One such ICP that has been studied extensively, both by our research group at The Aerospace Corporation⁷ and by others,^{8,9} is polyaniline (PANI). Moreover, recent literature¹⁰ has demonstrated that PANI can be synthesized into nanotubes and nanofibers using a template-free method. This novel way of making nanotubes is of considerable interest since these tubes are both organic and conductive and thus can be easily solubilized to aid in dispersion. It should be noted that electrical conductivity of these polymer tubes depends strongly on their degree of aggregation within a host. By maximizing their dispersion, a lower-volume fraction of these dark-green tubes is needed for inducing conductivity, which, in turn, maximizes the transmissivity and minimizes the solar absorptivity of these blends.

In this work, we present the synthesis of a new series of electrically conducting polymers in the form of microtubes and nanofibers that are generated through a self-assembly, template-free process and subsequently blended with a compliant, insulating host: polyurethane (PU). The influence of synthesis conditions on the morphology, size, and electrical properties of PANI tubes is investigated, and their respective blend properties are discussed.

2. Experimental

2.1 Starting Materials for PANI Tubes and Fibers

Aniline was purchased from Aldrich (99%) and doubly distilled in the presence of zinc under vacuum and polymerized immediately after distillation. All other chemicals were obtained from the indicated sources and used without further purification: ammonium persulfate (Aldrich, 99.99%), 2-naphthalenesulfonic acid (β -NSA) (TCI America, 97%), methanol (EM Sciences, 99.8%), and diethyl ether (EM Sciences, 99.9%).

2.2 Microtube and Nanofiber Polymerization

A typical polymerization for polyaniline microtubes is as follows: Into a 25-mL single-neck round-bottomed flask equipped with a magnetic Teflon-coated stirrer, 0.457 g (2.19 mmol) of β -NSA was added to 10 mL of deionized water. The mixture was stirred for 10 min at room temperature, and then 0.2 mL (2.19 mmol) of freshly distilled aniline was added to the acid solution. The aniline/acid complex was stirred vigorously for 15 min. An aqueous solution of ammonium persulfate (0.46 g in 5 mL of deionized water) was added to the white aniline complex and stirred for 24 h at room temperature. The polyaniline tubes were vacuum filtered using a Whatman #1 filter pad and subsequently washed with deionized water, methanol, and, finally, diethyl ether. The dark-green tubes were then placed in a vacuum oven at room temperature for 24 h to yield electrically conducting tubes. Nanofibers were synthesized using a similar method, but smaller mole ratios of monomer to dopant were incorporated into the polymerization.

2.3 Starting Materials for Polyurethane (PU)

All chemicals were purchased from Aldrich and were used as received unless noted otherwise. Toluene-2,4-diisocyanate (TDI) and 1,6 hexamethylenediisocyanate (HDI) were purified by distillation under reduced pressure. 3,3'-Dimethoxy-4,4'-biphenylenediisocyanate was recrystallized from ethyl acetate. N, N-Dimethylformamide (DMF) was purified by drying with anhydrous calcium sulfate, followed by distillation under reduced pressure.

2.4 Synthesis of Polyurethane (PU)

Polyurethanes were prepared according to a recent literature procedure¹¹ by a typical polyaddition between a diol and toluene-2,4-diisocyanate (TDI) or 1,6 hexamethylenediisocyanate (HDI) in a DMF solvent. Specifically, TDI (1.74 g, 0.01 mol) was slowly added to a solution of 3.60 g of diol (0.01 mol) in 40 mL of dry DMF. The resulting solution was degassed by a freeze-thaw process under vacuum and placed in an oil bath kept at 80°C. After heating for 6 h with stirring, the polyurethane was poured into 400 mL of cold water. The precipitated polymer was collected and reprecipitated from DMSO into methanol. The PU was dried in a vacuum oven for 24 h at room temperature.

2.5 Polymer Characterization

The chemical structures of both polyaniline tubes (PAT) and polyurethanes (PU) were identified by ^1H NMR (400 MHz Varian Unity INOVA, hexafluoroisopropanol (HFIP)- d_2) and FTIR (Nicolet, Magna 550). NMR chemical shifts of the PATs are given in the discussion section. Since the tubes were highly absorbing, they were examined by an internal reflection technique (attenuated total reflection, ATR) on the Nicolet using a germanium prism. Tube samples were analyzed by X-ray diffraction (XRD) using copper radiation and a computer-controlled Phillips Electronics Instruments model 3720 vertical powder diffractometer equipped with a monochromatic CuK α radiation X-ray source (1.54 Å, 40 kV, and 30 mA). Theta two-theta scans were run from 5°–80° two-theta with a step size of 0.02° 2 θ . The thermal behavior of PU material was examined by a TA 2910 DSC instrument. The DSC instrument was previously calibrated with indium. Typically, a 9–10 mg polymer film sample, contained in an aluminum non-hermetically sealed pan (previously vacuum dried at 70°C for 12 h), was placed in the DSC nitrogen-purged cell, which was initially at –10°C. A Hewlett Packard model 34401A multimeter (in four-point mode) was hooked up to a four-point-in-line dc conductivity apparatus to eliminate the contact resistance. Four nickel/silver, parallel-gold-coated, spring-loaded probes (40–70 g/tip spring force, by Interconnect Devices, Inc.) epoxied in a ceramic block with a 1.0-mm spacing were lowered via a micrometer so that they made direct contact with the film's surface. During the measurement, a constant current (typically 1 μA) was applied to the two outer probes, and the voltage across two inner probes was measured. Before measurement, the current was changed to ensure a linear V-I curve which indicates an Ohmic behavior. All resistance measurements were made in air at room temperature and converted to conductivity.

2.6 Film Preparation of PAT/PU Blends

Polyaniline tube/polyurethane blends were prepared by the following method: 5 mL of a 1% (wt/wt) solution of PU and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP, Aldrich) were stirred overnight at room temperature. To a 10-mL vial was charged a pre-measured amount of polyaniline tubes to yield the desired blend concentration. This mixture was stirred for exactly 1.5 min and cast onto a Teflon-coated glass substrate and subsequently covered with a recrystallization dish to allow for a slow evaporation (at room temperature) of HFIP solvent for a period of approximately 24 h. Samples were peeled off the Teflon substrate and placed in a vacuum oven for 24 h at 60°C.

3. Results and Discussion

3.1 Polyaniline Microtube Blends

The objective of this work was to advance the development of new electrically conducting polymers that can be blended with a compliant host that would yield optically transparent, low-color, conductive blends. Recent literature¹² has shown that organic conductive polymers such as polyaniline (PANI) can be solution blended into a variety of host polymers to yield robust, electrically conducting blends, but the characteristic deep green color imparted by the PANI guest would compromise the low-color objective needed to minimize solar absorptivity. One method to minimize this color is to modify the geometry of PANI from granular to tube shaped. Recently, Wan, et al.¹³ discovered a template-free method of synthesizing microtubules of conducting polymers by varying the polymerization conditions. This synthesis has proven effective in producing microtubules without the need to remove the polymer from a template. These new tubes attracted much attention because of their metal-like conductivity, inexpensive starting materials, and ease of synthesis using a template-free method. In addition, these tubes possess many unique characteristics that promise to induce higher electrical conductivity with minimal color, compared to the conducting polymers that are *granular*. Thus, the major objective in this task is to synthesize these tubes from a polymer known to be conductive and translate the properties of the resulting conducting polyaniline tubes into larger macro structures.

The template-free synthesis of polyaniline tubules was carried out in the presence of a large, bulky dopant, naphthalene sulfonic acid (β -NSA). Both FTIR and ^1H NMR were used to confirm that the polyaniline is the main backbone of the microtube. In Figure 1, FTIR clearly shows the signature

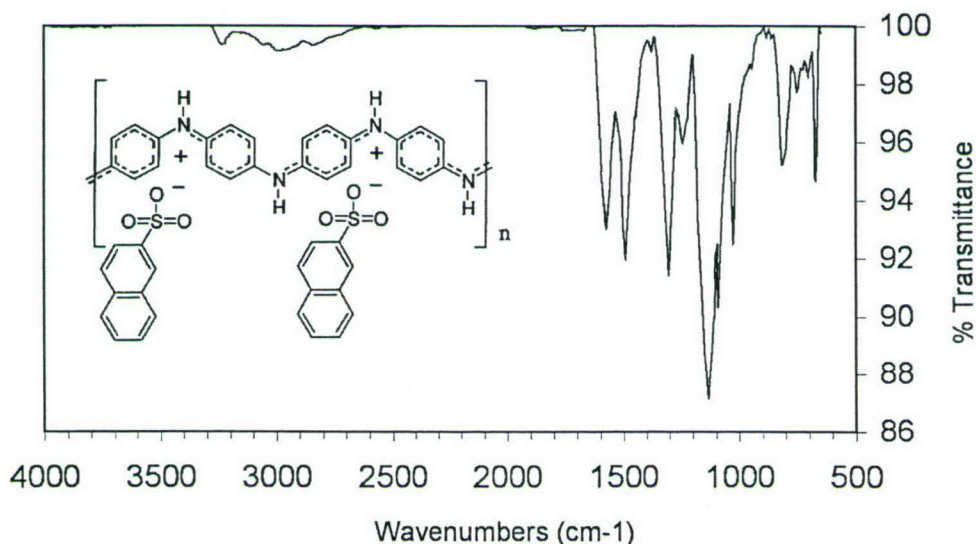


Figure 1. FTIR-ATR of PANI tubes with doping ratio [aniline]: [β -NSA] of 1:1.

PANI backbone with two strong absorbances at 1580 cm^{-1} and 1480 cm^{-1} due to the protonated quinoid ring stretching modes. In addition, the large absorbance at 1110 cm^{-1} corresponds to the C=N stretch of the protonated quinoid ring.

Further PANI confirmation is seen in the ^1H NMR spectra (Figure 2). The polyaniline tubes in deuterated HFIP solution exhibit multiplets at 7.2, 7.5, 7.7, and 7.8 ppm, which are attributed to the aromatic protons being deshielded by circulation of the nearby aromatic electrons of a neighboring PANI chain in each respective tube.

Powder wide-angle X-ray scattering (WAXS) showed that these microtubes lack any tight packing of the PANI chains that form the lining of the polymer tube. In Figure 3, the WAXS diffractograph shows a peak at $8^\circ 2\theta$ that corresponds to a d spacing of 1 nm. This peak may correspond to the distance between 2-D stacks of PANI chains separated by β -NSA counteranions. The smaller diffraction peaks at even lower scattering angles can be explained by some of the longer range order that exists between respective tubes. At higher scattering angles, a broad halo is seen at 20° and $27^\circ 2\theta$, which may be associated with the C=N=C linkages.

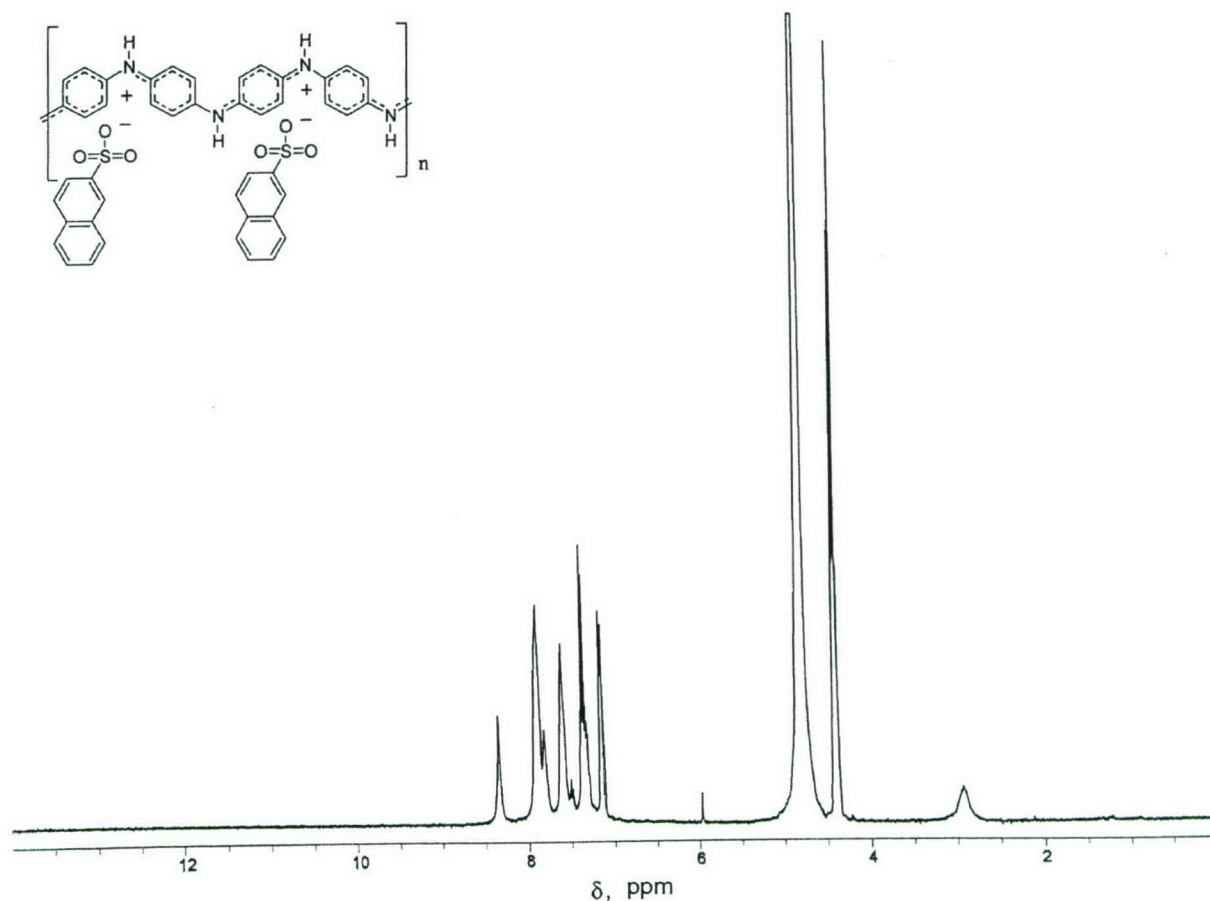


Figure 2. Proton nuclear magnetic resonance (^1H NMR) in deuterated hexafluoroisopropanol (HFIP- d_2) solution of PANI tubes with doping ratio [aniline]: [β -NSA] of 1:1.

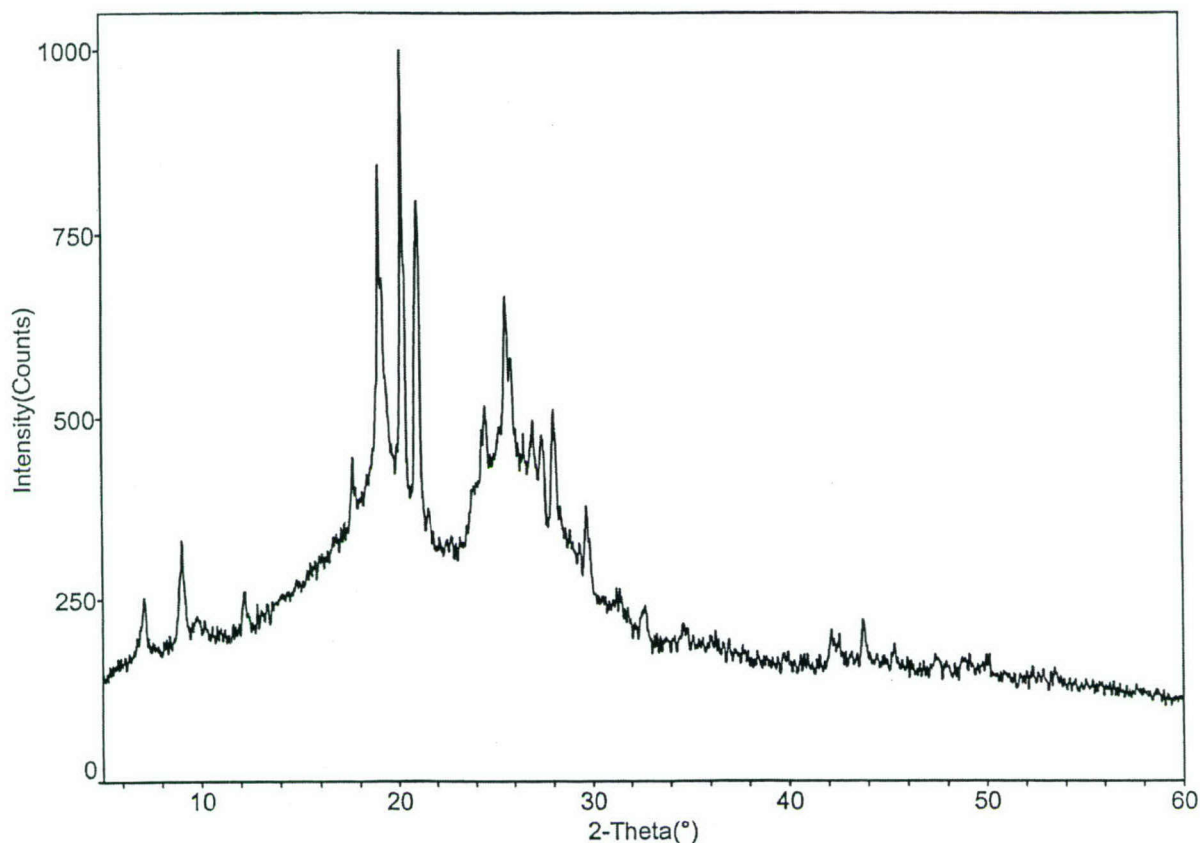


Figure 3. Wide-angle X-ray scattering (WAXS) of polyaniline microtubes with doping ratio [aniline]: [β -NSA] of 1:1.

The scanning electron micrographs revealed that the micro-sized tubes (Figure 4a) were hollow. Decreasing the molar doping level below the 1:2 ratio formed nanotubes with diameters ranging from 8 to 10 nm. Unlike the micro tubes where the tip and end of the tube were clearly defined, the nanostructures seen in Figures 4b and 4c had no real end or beginning in the tube length, and resembled more of a fibrous material than tubes.

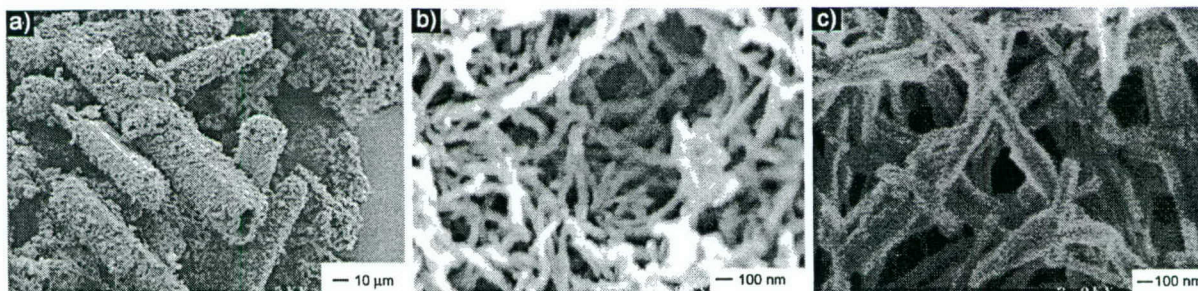


Figure 4. SEM images of PANI tubes doped with [aniline]:[β -NSA] doping ratios of (a) 1:2, (b) 1:0.50 and c) 1:0.25.

The electron micrographs in Figures 4a-c clearly show both tube formation of these chains and the relationship between molar doping ratios of β -NSA and tube diameter. There is much speculation as to how these conducting polymer chains form micro- and nanotubes without the aid of a "true" template. Generally speaking, the energetics for such tube formation have been shown to be minimal. Wan and Yang,¹⁴ the first to synthesis these novel materials, have proposed a pseudo-template model to explain the formation of the self-assembled tubes. They suggest that micelles are formed by combining the hydrophobic aniline monomer with the hydrophilic dopant, β -NSA. The formed micelles of the [aniline]:[β -NSA] play a role in forming a pseudo template that facilitates nano- and micro-structures of PANI- β -NSA. Thus, an increase in doping level promotes a higher level of template formation and larger tubes, which was confirmed by our experiments. However, an aniline monomer with a dipole moment (μ) of 1.13 D is not hydrophobic; rather, its dipole moment is similar to water's value of 1.9 D. The existence and role of micelles as temporary templates in the polymerization method is overestimated. Rather, it is thought that the formation of these tubular structures lies in both the surfactant function of the aromatic dopant, combined with the low energetics of aniline to polymerize in a helical fashion, which would form the skeleton of the PANI tube. Clearly, more work needs to be done in this area to elucidate the formation mechanism.

As seen in Figure 5, the molar doping ratio of aniline to dopant significantly affected the diameter of the tubes. Increasing dopant concentration beyond parity with aniline increased the diameter size from nano to micro. The values of room-temperature electrical dc conductivity PAT ranged from 0.08 to 1 S/cm, showing some dependency on the dopant level. However, it should be noted that samples from each doping ratio were pressed together in a KBr pellet press, and thus these values were an average of the compressed tubes. The large gaps that form between the tubes are hopping barriers for the charge carrier and thus reduce the delocalization of the carrier to yield low conductivity values. We are presently trying to measure the intrinsic dc conductivity of the microtubes to better understand the relationship between tube diameter and electrical conductivity.

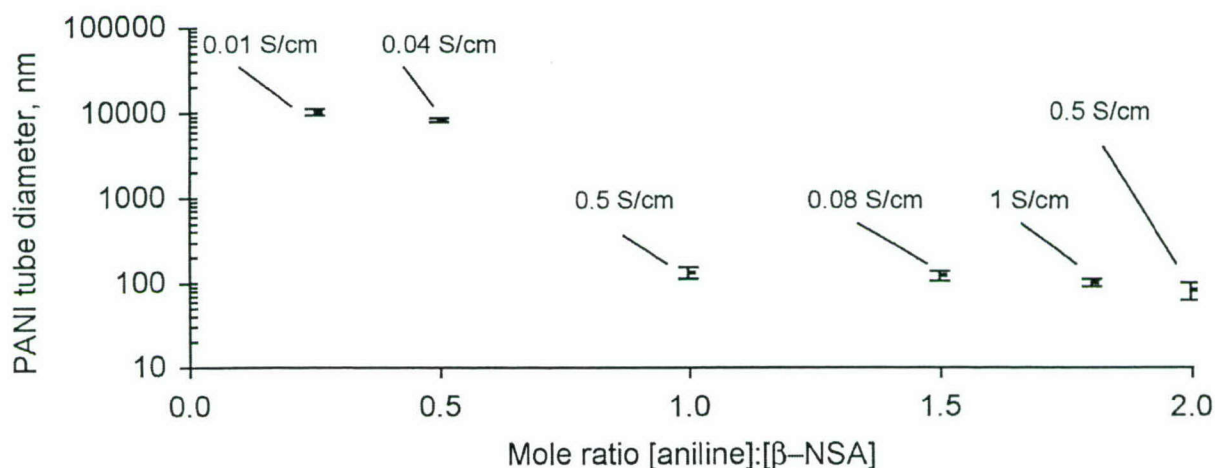


Figure 5. PANI nanotube diameter as a function of mole ratio of aniline monomer to dopant, with error bars indicating diameter variation.

3.2 Polyaniline Microtube/Polyurethane Blends

In addition to the micro- and nanotube synthesis, a low-glass-transition-temperature (5°C) polyurethane was synthesized to demonstrate that the PANI tubes can be solution-blended with the insulating PU host in a mutual solvent (HFIP) to form an intrinsically conducting compliant blend. This method of solution-blending PANI microtubes is currently the most efficient way of processing PATs into an insulating host system. Maximum electrical conductivities at room temperature (σ_r) of the PANI microtube blends (using the 10- μm -dia tubes) were $1 \times 10^{-5} \text{ S/cm}$ and $1 \times 10^{-3} \text{ S/cm}$ for 0.5% and 2 % (wt/wt) PANI microtube loading, respectively. These values are sufficient for the minimal value needed ($1 \times 10^{-6} \text{ S/cm}$) for charge mitigation.¹⁵ As seen in Figure 6, the PANI microtubes were easily dispersed in the PU and yielded fairly transmissive blends when cast from solution.

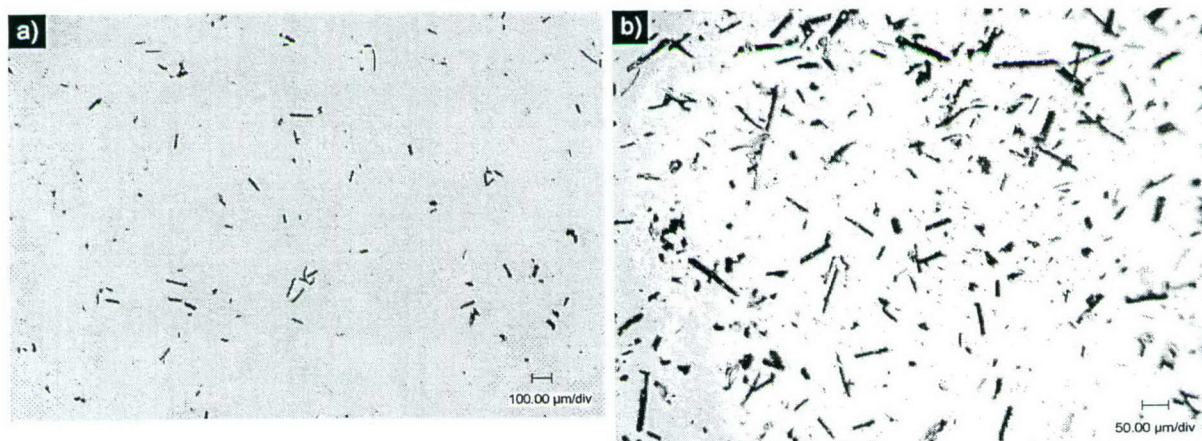


Figure 6. Optical micrograph of (a) 0.5 % and (b) 2 % (wt/wt) blend of polyaniline microtubes (dark regions) imbedded in a polyurethane host.

4. Conclusion

Self-assembled polyaniline micro/nanotubes were synthesized by a template-free method in the presence of an organic acid that acts as a doping material. Changing the molar doping level ratio controls the diameters of these polyaniline tubes. Bulk conductivity of the tubes was demonstrated for both micro- and nanotubes. When microtubes were solution-blended with polyurethane, a highly dispersed fractal network of tubes was observed, and the resulting blend conductivity was sufficient for charge mitigation. The promising results of this program lend themselves to developing an all-polymer microtube-conducting composite that has sufficient conductivity for mitigation of electrical charge. The prospects for direct application of these polymeric microtubes for dissipating charge on deployable materials have been improved with the aid of characterization of the polyaniline tubes and resulting blends. Future work will emphasize decreasing the tube size and increasing dispersion to improve both the mechanical properties and conductivity of these materials.

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